December 29, 1961
DMIC Memorandum 144

A REVIEW OF RECENT DEVELOPMENTS IN TITANIUM AND TITANIUM ALLOY TECHNOLOGY

DEFENSE METALS INFORMATION CENTER
BATTELLE MEMORIAL INSTITUTE
COLUMBUS 1, OHIO

62-1-4

A REVIEW OF RECENT DEVELOPMENTS
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This memorandum briefly summarizes recent developments in titanium metallurgy that became known to the DMIC during the period from September to mid-December, 1961. There has been little in the way of truly significant developments in this field during this period. However, several very interesting reports have come out describing developments in such diverse areas as the reactivity of titanium with nitrogen tetroxide, and high-energy-rate extrusion requirements. The principal conclusions from selected studies are presented.

A study of the air contamination and protection for four DOD titanium sheet alloys was recently completed at the TMCA facilities in Nevada.(1)** The research indicated that Ti-4Al-3Mo-1V and Ti-6Al-4V had about equal resistance to penetration by interstitial contaminants. The hardness penetration tests showed Ti-13V-11Cr-3Al and Ti-2.5Al-16V alloys had lower resistance to contamination in that order. With regard to metal loss during exposure to elevated temperature, the alloys also were graded in the above order. Commercial or purified helium and argon were equally effective in preventing contamination, and mixtures of carbon monoxide with the inert gases were also effective. The lead-silicate glass called "Anhydralin" protected the titanium alloys below 1900 F. However, other molten salts (NaCl, LiCl, and KF) corroded these alloys so rapidly that they were useless as protective media.

The Ti-5Al-2.5Sn, Ti-6Al-4V, and Ti-13V-11Cr-3Al alloys were evaluated at Convair Astronautics for susceptibility to hydrogen embrittlement induced by chemically milling in a hydrofluoric acid bath.(2) The all-alpha Ti-5Al-2.5Sn alloy was not embrittled by chem-milling in this media as determined by constant-strain-rate bend tests. The Ti-6Al-4V alloy was only slightly embrittled, while the Ti-13V-11Cr-3Al alloy was severely embrittled.

An investigation concerning the titanium-LOX reaction was conducted by using high-pressure gaseous oxygen at Battelle Memorial Institute.(3) (The mechanism for the titanium-LOX reaction proposed in a previous study, WADD TR 60-258, suggested that the impact of a titanium surface immersed in LOX generates sufficient heat to gasify a pocket of oxygen.) The recent study established that a fresh titanium surface would react with gaseous oxygen under about 100-psig pressure at temperatures between -250 F and room temperature. At the higher temperatures, the threshold pressure for a reaction is lowered (50 to 75 psig for -50 F to room temperature). In the temperature range studied, the Ti-6Al-4V alloy requires a slightly higher pressure to support the reaction than does unalloyed titanium. Additional investigations to determine how to minimize the reaction indicated that a 5 per cent HF or argon dilution of the gaseous oxygen reduced the chemical reactivity. Fluoride-phosphate or aluminum coatings did not affect the reactivity in gas but afforded some protection to titanium during impact under LOX.

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In work of a similar character at the Allied Chemical Corporation(4), it was found that unalloyed titanium and Ti-6Al-4V alloy ignite about 50 per cent of the time in liquid nitrogen tetroxide (N_2O_4) when impacted with a 0.5-inch diameter flat striker having an energy of 200 ft-lb. Storage of the unalloyed grade in N_2O_4 decreases the energy required for 50 per cent ignition to 60-70 ft-lb, while the sensitivity of the 6Al-4V grade is unaffected.

Two vacuum-fusion methods and an inert-gas fusion method satisfactory for the determination of oxygen (0.02 to 1.00 per cent range) in titanium are described in a Bureau of Mines paper(5). While the main portion of the paper is devoted to the description of these methods, a résumé of other suggested methods for analyzing titanium for oxygen also is given.

The mechanical properties of the Ti-5Al-2.5Sn alloy at -423 F (liquid-hydrogen temperature) as affected by the common impurities, iron and oxygen, were determined recently at Convair Astronautics.(6) The data show increased strengths and decreased toughness for the high-iron and high-oxygen heats. Based on these tests, it appeared that the Ti-5Al-2.5Sn alloy should contain no more than 0.12 per cent oxygen and 0.25 per cent iron in order to retain adequate toughness at liquid-hydrogen temperatures.

In studies completed by Watertown Arsenal, it was found that high-strength sheet materials could be satisfactorily tested for toughness by using an edge-notch specimen similar to the standard V-notch Charpy specimen except for thickness.(7) Precracking the more brittle materials by either reverse bending or fatigue techniques resulted in the generation of quantitative fracture toughness values. The precracked sheet Charpy data are expressed in terms of energy to propagate per unit of crack area (W/A), and the results expressed in in.-lb/in.^{2} are comparable with G_c values. The work also indicated the effect of strain rate on fracture toughness. Many high-strength sheet materials exhibit enhanced fracture-toughness properties under impact-loading conditions. It was found, however, that Ti-13V-11Cr-3Al was an important exception. The all-beta titanium grade (solution-treated condition) exhibited much greater fracture toughness in slow bend than in impact tests.

What appears to be an improvement in the technique for the Charpy impact testing of sheet materials was reported from Watertown Arsenal.(8) Tests were conducted on standard and reduced-thickness Ti-5Al-1.5Fe-1.4Cr-1.2Mo specimens heat treated to various strength levels. The thin specimens were tested by simply cementing them together in pairs with spacers between them to form an impact specimen of standard thickness. This arrangement permits impact testing of sheet without adjustments to the apparatus. The Watertown tests revealed a nonlinear relationship between thickness of specimen and Charpy impact values and a temperature effect. The nonlinearity is more prominent at high temperatures, with the thicker specimens absorbing considerably more impact energy.

Flatness has long been a problem in the manufacture of titanium alloy sheet. In a report from the Crucible Steel Company, several methods of producing flat solution-treated titanium alloy sheet are reviewed and a new concept is described.(9) Basically, the new method involves heating and cooling the sheet under tension. The results of the work indicate that the DOD alloys, Ti-6Al-4V, Ti-4Al-3Mo-1V, Ti-2.5Al-16V, and Ti-3Al-6Mo, can be produced with an out-of-flatness range of between 1 to 2 per cent.

The Republic Aviation Corporation reports on extrusion techniques for Ti-7Al-4Mo alloy.(10) Several billets were coated with glass lubricants to determine billet contamination in 1800 F exposure for heat-soak times of 45 and 90 minutes. The microhardness survey indicated that a 383A glass results in less reactivity with titanium than do 85 or A-40 glass compositions and that most of the contamination occurs during the first 45 minutes of exposure. The program involves the experimental extrusion and straightening of several structural shapes (channels, tees, and angles) for advanced airframe designs.

An investigation into the parameters associated with Dynapak extrusion is in progress at Westinghouse Electric Corporation.(11) Lubrication, die and billet geometry, reduction ratio, and temperature problems are being researched. Among other materials, Ti-6Al-4V alloy has been experimentally extruded (50 mil "T" section), and the power requirements to extrude this material by high-energy-rate techniques are presented. Some difficulties with heat build-up, even when using moderately low extrusion temperatures, were encountered.

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(11) Rieppel, J. M., Westinghouse Electric Corporation, Blairsville, Pennsylvania, preliminary information under an Air Force contract.

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119	The Emittance of Iron, Nickel, Cobalt and Their Alloys, July 25, 1961, (AD 261336 $2.25)
120	Review of Recent Developments on Oxidation-Resistant Coatings for Refractory Metals, July 31, 1961, (AD 261293 $0.50)
121	Fabricating and Machining Practices for the All-Beta Titanium Alloy, August 3, 1961, (AD 262496 $0.50)
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123	Review of Recent Developments in the Technology of Beryllium, August 18, 1961, (AD 262497 $0.50)
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126	A Review of Recent Developments in Titanium and Titanium Alloy Technology, September 15, 1961
127	Review of Recent Developments in the Technology of Tungsten, September 22, 1961
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131	Review of Recent Developments in the Technology of High-Strength Stainless Steels, October 13, 1961
132	Review of Recent Developments in the Metallurgy of High-Strength Steels, October 20, 1961
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134	Machining of Superalloys and Refractory Metals, October 27, 1961
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137	Review of Recent Developments on Oxidation-Resistant Coatings for Refractory Metals, November 8, 1961
138	Review of Recent Developments in the Technology of Beryllium, November 16, 1961
139	Review of Recent Developments in the Technology of Tungsten, November 24, 1961
140	Review of Recent Developments in Metals Joining, December 6, 1961
141	The Emittance of Chromium, Columbium, Molybdenum, Tantalum, and Tungsten, December 10, 1961